

SPECIFICATION

PROCESSING METHOD FOR INDIGO-DYED CLOTH AND INDIGO-DYED
CLOTH PROCESSED BY SUCH A METHOD

5 TECHNICAL FIELD

The present invention relates to a processing method for an indigo-dyed cloth and the indigo-dyed cloth processed by such a method.

BACKGROUND ART

10 So-called indigo-dyed goods dyed by indigo dyes, which include goods dyed by using Japanese indigo plant, exhibit comparatively clear color tones immediately after the dyeing process; however, it has been known that after having been preserved or used for a long time, for example,
15 from ten years to several tens of years, those goods having a comparatively high dyeing density gradually come to have deep, calm color tones with blue-black colors, while those goods having a comparatively low dyeing density gradually come to have deep, calm color tones with yellowish colors.

20 In recent years, there have been demands among the users for such deep, calm color tones, that is, so-called vintage colors, in denim articles, and there have been rapidly increasing demands for such denim articles having vintage colors. In an attempt to obtain the denim articles having
25 vintage colors, actual preservation of denim articles for a

long time fails to ensure a sufficient supply, and there have been demands for a method by which vintage colors are applied to denim articles in a comparatively short period of time.

5 Conventionally, in the manufacturing process for denim articles, only the warp yarn is dyed by using an indigo dye prior to formation of the cloth. In this case, color tones, derived from indigo-dye and yellow-dye, are added to the warp yarn by using an indigo dye and a yellow dye, such as
10 a sulfur dye and a vat dye, in combination with each other, and by using the warp yarn dyed as described above, attempts have been made to add the vintage color to the surface side of a denim article on which the warp yarn appear mostly. In this technique, however, the yellow dye
15 is subjected to crocking during the succeeding rinsing process and the like to contaminate the filling yarn, resulting in a sense of incongruity in that the use of a yellow dye is clearly found by the resulting color tone; therefore, it is not possible to sufficiently reproduce the
20 inherent vintage color.

 Moreover, in order to add vintage colors to denim articles in a comparatively short period of time, a method in which after a cloth has been formed by using the warp yarn dyed by only an indigo dye, the entire cloth is
25 overdyed by using a yellow dye or in which after an article

has been produced, the entire article is overdyed by using the yellow dye, has been proposed. However, since the filling yarn is dyed simultaneously, this technique also results in a sense of incongruity in that the use of a yellow dye is clearly found by the resulting color tone; consequently, it is not possible to sufficiently reproduce the inherent vintage color.

For this reason, Japanese Patent Application Laid-Open No. 11-200261 has disclosed a processing method for a cotton product such as jeans in which after allowing nitric acid to react with the cotton product such as jeans or the cloth thereof, the resulting product is neutralized by a basic substance. However, the application of this method to a denim cloth has also failed to sufficiently reproduce the inherent vintage color. Moreover, even when the vintage color is successfully added to the denim article, the resulting color is easily erased during post-processes such as a washing process. Furthermore, the dyeing density derived from the indigo dye tends to drop abruptly, making it difficult to set the dyeing density of the indigo dye at a comparatively high level.

DISCLOSURE OF INVENTION

The present invention has been devised to solve the above-mentioned problems, and its objective is to provide a processing method for an indigo-dyed cloth which makes it

possible to add a vintage color that is equivalent to the vintage color of an indigo-dyed cloth that has been actually preserved or used for a long time, and is also less susceptible to disappearance even by a washing process, in a comparatively short period of time, and an indigo-dyed cloth to which such a vintage color is added.

The present invention relates to a processing method for an indigo-dyed cloth in which a nitrogen-based oxidizing agent is applied to an indigo-dyed cloth and the resulting cloth is subjected to a heating process, and an indigo-dyed cloth processed by such a method.

BEST MODE FOR CARRYING OUT THE INVENTION

In the processing method for an indigo-dyed cloth of the present invention, a nitrogen-based oxidizing agent is applied to an indigo-dyed cloth (nitrogen-based oxidizing agent applying process).

An indigo-dyed cloth to be used in the method of the present invention is a cloth at least one portion of which is dyed by a synthesized or natural indigo dye. In the present invention, the portion, dyed by the indigo dye, is allowed to have a vintage color that is equivalent to the vintage color of an indigo-dyed cloth that has been actually preserved or used for a long time, and is less susceptible to disappearance even by a washing process.

In the present specification, the term "cloth" is used

as a concept which, not limited to a form on the plane such as fabric, knit and nonwoven fabric, includes forms of products of these (for example, jeans) and forms of fibers and yarns formed by twisting multiple fibers.

5 With respect to the fiber that forms a cloth, not particularly limited as long as it can be dyed by an indigo dye, examples thereof include cellulose-based natural fibers (cotton, hemp, etc.), cellulose-based recycled fibers (Rayon, cupra, etc.), cellulose-based semi-
10 synthesized fibers (acetate, etc.) and blends of these with synthetic fibers.

 In the present invention, in particular, so-called denim, which has a twill arrangement in which a cotton yarn dyed by an indigo dye is used as the warp yarn while a non-
15 dyed cotton yarn (raw yarn) is used as the filling yarn, with the warp yarn predominantly appearing on the surface side, is preferably used from the viewpoint of providing a superior vintage color.

 In the case when the denim is used, those denims that
20 have been subjected to conventionally known treatments, which will be described later, such as a singeing treatment, a rinsing treatment, a skewing treatment, a preshrinking treatment and a washing treatment, may be used, or those untreated denims immediately after the weaving process may
25 be used, and from the viewpoint of effectively adding the

vintage color evenly, those denims that have been subjected to the singeing treatment, rinsing treatment, skewing treatment and preshrinking treatment are preferably used. The washing treatment process is generally carried out after the treatment processes of the present invention. Here, in the case when the untreated denims are used, after the treatment processes of the present invention have been carried out, conventionally known treatment processes may be carried out.

The nitrogen-based oxidizing agent to be used in the present invention is an oxidizing agent that is capable of oxidizing an indigo dye and of generating a nitrogen oxide in the succeeding nitrogen-oxide generating process. Examples of the nitrogen-based oxidizing agent include: nitrate, nitric acid, ammonium nitrate, nitrite, nitrous acid and ammonium nitrite. In the present invention, since such an oxidizing agent capable of not only oxidizing an indigo dye, but also generating a nitrogen oxide in the post process, is used, it becomes possible to add a vintage color that is equivalent to the vintage color of an indigo-dyed cloth that has been actually preserved or used for a long time, and is also less susceptible to disappearance even by a washing process. Although the mechanism for achieving such a superior vintage color has not been clarified in detail, it is considered that a specific

oxidizing agent (nitrogen-based oxidizing agent) is used so that a nitrogen oxide, generated through the post treatment, exerts a unique reaction on the indigo dye to prepare a superior vintage color.

5 In the case when, without using such a nitrogen-based oxidizing agent, another oxidizing agent, such as potassium manganese peroxide, hypochlorous acid soda, ozone and hydrogen peroxide, is used, it is not possible to add a superior vintage color to the cloth, and even when a
10 vintage color is added thereto, the vintage color is easily erased during post-processes such as a washing process.

 More specifically, with respect to the nitrogen-based oxidizing agent, specific examples of nitrate include: nitrates of heavy metal, such as zinc nitrate, lead nitrate,
15 iron nitrate, copper nitrate and manganese nitrate; nitrates of alkali metal, such as sodium nitrate and potassium nitrate; and nitrates of alkali earth metal, such as magnesium nitrate, calcium nitrate and barium nitrate.

 Specific examples of nitrite include nitrites of heavy
20 metal, such as zinc nitrite; nitrites of alkali metal, such as sodium nitrite and potassium nitrite; and nitrites of alkali earth metal, such as magnesium nitrite and calcium nitrite.

 In the case when a nitrate or a nitrite is used, the
25 cloth to which a vintage color is added by the method of

the present invention is allowed to have a residual compound containing metal that formed the salt. For example, in the case when zinc nitrate is used as the nitrogen-based oxidizing agent, residual zinc oxide is
5 contained in the cloth.

In order to achieve a superior vintage color and also to provide availability thereof, among the above-mentioned nitrogen-based oxidizing agents, nitrates of heavy metal, nitric acid, ammonium nitrate, nitrites of alkali metal are
10 preferably used; nitrates of heavy metal and ammonium nitrate are more preferably used; and zinc nitrate is most preferably used.

Upon applying the nitrogen-based oxidizing agent to a cloth, the nitrogen-based oxidizing agent is preferably
15 placed evenly on the cloth or more preferably placed evenly between yarns or fibers that constitute the cloth; and, for example, ① a nitrogen-based oxidizing agent aqueous solution may be applied to the cloth so that the cloth is impregnated with the aqueous solution; or ② the cloth is
20 immersed in the aqueous solution and squeezed so that the cloth may be impregnated with the aqueous solution; or ③ the nitrogen-based oxidizing agent may be dusted over the cloth; and in order to add a superior vintage color thereto, the above-mentioned method ① or ② is preferably used. In
25 particular, in the case when denim is used as the cloth, it

is only necessary to add the vintage color onto the surface side of the denim; therefore, from the viewpoint of reducing the amount of the aqueous solution required for the process, preferably, the above-mentioned aqueous solution is applied only onto the surface side of the denim by using the above-mentioned method ①. Moreover, the application of the above-mentioned method ① makes it possible to avoid a slight reduction in the cloth strength.

In the case when the aqueous solution of a nitrogen-based oxidizing agent is used, the concentration of the nitrogen-based oxidizing agent in the aqueous solution is not particularly limited, as long as a vintage color is added to the cloth, and is normally set in a range from 15 g/L to 200 g/L. With respect to the nitrogen oxide, two or more kinds of the above-mentioned compounds may be used in combination as long as a superior vintage color is achieved, and in this case, the total concentration of these compounds is preferably adjusted within the above-mentioned range.

Not particularly limited, the temperature of the aqueous solution may be set at room temperature, or the aqueous solution may be heated so as to accelerate dissolution of the nitrogen-based oxidizing agent to water; and from the viewpoint of a reduction in production costs, it is preferably set at room temperature.

Additives such as a penetrating agent and a thickener may be added to the nitrogen-based oxidizing agent aqueous solution on demand.

In the case when the above-mentioned method ② is adopted, the penetrating agent is used as an additive for accelerating impregnation of the nitrogen-based oxidizing agent aqueous solution into the cloth; and, for example, an anionic or nonionic surfactant or the like is applicable.

In the case when the above-mentioned method ① is adopted, upon applying a nitrogen-based oxidizing agent aqueous solution by using a doctor-type coating machine or the like, the thickener serves as an additive to make the coating process easier; and, for example, a methyl cellulose-based thickener, a methyl starch-based thickener or the like may be used.

In the above-mentioned method ①, the amount of application of the aqueous solution is not particularly limited as long as a vintage color can be added to the cloth, and in the case when a denim of about 450 g/m^2 is used, the amount is normally set to not less than 50 g/m^2 , preferably, in a range from 100 to 180 g/m^2 . When the amount of application is too small, the vintage color to be added becomes too thin, failing to actually exert the effects of the present invention. When the amount of application is too great, the dyeing density of the indigo

dye tends to be lowered.

In the above-mentioned method ②, the squeezing rate is not particularly limited as long as a vintage color can be added to the cloth; and, for example, in the case when a
5 denim of about 450 g/m^2 is used, the rate is normally set to not less than 50 %, preferably, in a range from 50 to 80 %. The squeezing rate refers to a rate of "the weight of an aqueous solution that has been impregnated in the cloth immediately after the squeezing process" to "the
10 weight of a dried cloth before the process." When the squeezing rate is too small, the vintage color to be added becomes too thin, failing to actually exert the effects of the present invention. When the squeezing rate is too great, the dyeing density of the indigo dye tends to be
15 lowered. Moreover, the strength of the cloth tends to be lowered.

Immediately after applying the nitrogen-based oxidizing agent to the cloth, the resulting cloth may be subjected to the next process (nitrogen oxide generating
20 process), or may be once dried. The drying process may be carried in a degree so as to ensure a preferable transporting property of the cloth to the next process; and, for example, the drying process may be achieved by maintaining the cloth at a temperature range from 60 to
25 120°C for 1 to 10 minutes, or by leaving the cloth at room

temperature.

In the present invention, the cloth to which the nitrogen-based oxidizing agent has been applied is then subjected to a process in which a nitrogen oxide is generated (nitrogen oxide generating process).

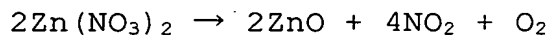
The process in which a nitrogen oxide is generated refers to a process that is capable of generating NO_x (for example, N₂O, N₂O₃, NO₂, N₂O₄, N₂O₅, NO₃ and N₂O₆, preferably, NO₂ and N₂O, more preferably, NO₂ or the like) from the nitrogen-based oxidizing agent applied to a cloth, and, for example, a heating treatment is proposed.

Upon carrying out the heating process, a conventionally known heating means can be applied as long as the following treatment temperature and treatment time are maintained; and, for example, a roller-type baking machine, a pin-tenter type heat setter or the like may be used.

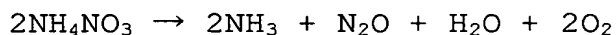
The treatment temperature and treatment time are not particularly limited as long as a nitrogen oxide is generated from the nitrogen-based oxidizing agent, and preferably set, for example, normally in a temperature range of 100 to 220°C for 0.5 to 2 minutes.

For example, it is considered that in the case when the heating treatment of the present process is carried out by using zinc nitrate as the nitrogen-based oxidizing agent,

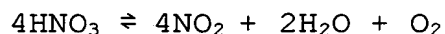
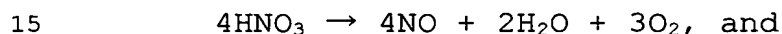
NO₂ is generated based upon the following chemical reaction formula:



Moreover, for example, it is considered that in the case when the heating treatment of the present process is carried out by using ammonium nitrate as the nitrogen-based oxidizing agent, N₂O is generated based upon the following chemical reaction formula:



Furthermore, for example, it is considered that in the case when the heating treatment of the present process is carried out by using nitric acid as the nitrogen-based oxidizing agent, NO and NO₂ are generated based upon the following chemical reaction formulas:



By carrying out the processing method of the present invention as described above, the portion, dyed by the indigo dye, is allowed to have a vintage color, and the cloth having a comparatively high dyeing density in the indigo dye is allowed to have a deep, calm vintage color with a blue-black tone, while the cloth having a comparatively low dyeing density is allowed to have a deep, calm vintage color with a yellowish tone.

Normally, in the processing method of the present

invention, a denim article, which has a comparatively high dyeing density in an indigo dye, is used so that a vintage color with a blue-black tone is achieved. The vintage color to be achieved by the present invention can be
5 desirably adjusted in a range from blue-black tone to yellowish tone by changing processing conditions (such as the concentration of nitrogen-based oxidizing agent, and the temperature and time of the heating treatment). In other words, the higher the concentration of the nitrogen-
10 based oxidizing agent, the closer to yellowish tone the vintage color becomes. The higher the heating temperature, the closer to yellowish tone the vintage color becomes. The longer the heating time, the closer to yellowish tone the vintage color becomes.

15 With respect to known treatments that may be applied to a cloth, in particular, a denim article, before or after the processing method (the applying process and the nitrogen-oxide generating process) of the present invention, for example, treatments, such as a singeing treatment, a
20 rinsing treatment, a skewing treatment, a preshrinking treatment and a washing treatment, are proposed. The following description briefly discusses these treatments.

The singeing treatment is a process in which fluff on the cloth surface is burned and removed to prepare a flat
25 surface so that the cloth texture is clarified to provide a

good appearance, and, more specifically, the singeing process is carried out by using a singeing machine of a hot-plate type, an electrothermic type or a gas flame type.

5 The rinsing treatment is a process for softening the cloth, and, more specifically, a warm aqueous solution containing various softeners is absorbed in the cloth and the cloth is then dried.

10 The skewing treatment is a process in which by preliminarily skewing the cloth prior to the washing process, the cloth is prevented from being further skewed during the washing process. Since a cloth having a twill structure immediately after the weaving process exerts a skewing property when washed, this treatment is used. For example, a known skew control device or weft straightner
15 may be used.

The preshrinking treatment is a process in which prior to a washing process, the cloth is preliminarily shrunk to a certain degree so that the shrinkage due to the washing process is reduced. Since a cloth having a twill structure
20 immediately after the weaving process exerts a shrinking property when washed, this treatment is applied. For example, a known compressive shrinking device may be used.

The washing treatment is a known process which processes a cloth, in particular, a denim fabric, so as to
25 have a desired color and handle; and, for example,

treatments, such as a hot-water treatment, an enzymatic treatment and a stone-washing treatment, are proposed. These treatments are normally carried out immediately before finishing the product or after finishing the product, and are mainly carried out after finishing the product. Here, an overdyeing process and a bleach-out process may be carried out immediately before or immediately after the washing treatment.

EXAMPLES

Example 1

A denim article (AIJ23599; made by Kurabo Industries Ltd., cloth weight: 460 g/m²) was subjected to a singeing treatment, a rinsing treatment, a skewing treatment and a preshrinking treatment. Then, an aqueous solution containing zinc nitrate hexahydrate having a concentration of 100 g/L and a methyl cellulose-based thickener having a concentration of 6 g/L was applied onto the surface side of the denim article so that the amount of coat was set to 160 g per one square meter by using a doctor-type coating machine, and after this had been dried, the resulting denim article was subjected to a heating process at 180°C for 2 minutes by using a baking machine.

Example 2

A denim article (AIJ23599; made by Kurabo Industries Ltd., cloth weight: 460 g/m²) was subjected to a singeing

treatment, and impregnated with an aqueous solution containing zinc nitrate hexahydrate having a concentration of 150 g/L and a nonionic penetrating agent having a concentration of 3 g/L at a squeezing rate of 60 %, and
5 dried by using a continuous padder; and the resulting denim article was then subjected to a heating process at 180°C for 2 minutes by using a baking machine.

Example 3

A denim article was processed in the same manner as
10 example 1, except that the aqueous solution for applying was changed to an ammonium nitrate aqueous solution having a concentration of 130 g/L and that the resulting denim article was subjected to a heating process at 210°C for 2 minutes.

15 Example 4

A denim article was processed in the same manner as example 1, except that the aqueous solution for applying was changed to a nitric acid aqueous solution having a concentration of 20 g/L and that the resulting denim
20 article was subjected to a heating process at 170°C for 2 minutes.

Example 5

A denim article was processed in the same manner as example 1, except that the aqueous solution for applying
25 was changed to a sodium nitrite aqueous solution having a

concentration of 150 g/L and that the resulting denim article was subjected to a heating process at 210°C for 2 minutes.

Comparative example 1

5 A denim article was processed in the same manner as example 1, except that the aqueous solution for applying was changed to an industrial sodium hypochlorite (effective chlorine 11 %) aqueous solution having a concentration of 300 g/L, and that the applying process was carried out by
10 using a brush.

Comparative example 2

 A denim article was processed in the same manner as example 1, except that the aqueous solution for applying was changed to a potassium permanganate aqueous solution
15 having a concentration of 10 g/L, that the resulting denim article was subjected to a heating process at 140°C for 2 minutes, that the denim article having been heated was washed by using acidic sodium sulfite, and that the
 applying process was carried out by using a brush.

20 When each of the denim articles obtained through the above-mentioned Examples was visually observed, it was found that all the denim articles were allowed to have a deep, calm vintage color with a blue-black tone that was equivalent to an indigo-dyed cloth that had been actually
25 preserved for a long time. When each of these denim

articles was washed once by using a household washing machine, it was found that all the denim articles were allowed to have a deep, calm vintage color with a yellowish tone that was equivalent to an indigo-dyed cloth that had been actually preserved for a long time. Moreover, when each of these was further washed ten times by using a household washing machine, the vintage color with a yellowish tone was not erased. Furthermore, even when these denim articles were bleached out by using sodium hypochlorite, the vintage color was not erased.

When each of the denim articles obtained through the above-mentioned Comparative examples was visually observed, it was found that each of the denim articles did not have a deep, calm vintage color with a blue-black tone. Even when each of these denim articles was washed once by using a household washing machine, each of the denim articles did not exhibit a deep, calm vintage color with a yellowish tone.

These denim articles (washed once) were visually evaluated with respect to the vintage color. The evaluation processes were carried out by giving points ranging from "5" to "1". The higher the point, the better (deeper, calmer) the vintage color becomes. In the present invention, the level of "2" or higher indicates a range that causes no problem in practical use.

Table 1

	Evaluation
Example 1	5
Example 2	4
Example 3	4
Example 4	2
Example 5	2
Comparative Example 1	1
Comparative Example 2	1

INDUSTRIAL APPLICABILITY

The method of the present invention makes it possible
5 to add to an indigo-dyed cloth (in particular, denim) a
vintage color that is equivalent to the vintage color of an
indigo-dyed cloth (in particular, denim) that has been
actually preserved or used for a long time, in a
comparatively short period of time. Moreover, by altering
10 the processing conditions (such as the concentration of a
nitrogen-based oxidizing agent, the temperature and time of
the heating treatment), it becomes possible to desirably
adjust the vintage color within a range from blue-black
tone to yellowish tone. The vintage color, obtained by the
15 method of the present invention, is hardly erased even by
washing processes.